Preliminary investigation into lithium extraction by phosphoric acid leaching of spodumene

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ABSTRACT

Demand for lithium has risen significantly with the prevalence of lithium-ion batteries in renewable energy technology. Spodumene is the primary lithium-bearing mineral of interest, due to its comparatively high grade and simple composition. However, methods for lithium extraction from spodumene remain complex. In this study, phosphoric acid was investigated as an alternative leaching agent. Preliminary leach experiments were performed on 1 g samples of pure β-spodumene with varying acid concentration, temperature, residence time and liquid to solid ratio. Chemical analysis of the leach filtrates and residues by inductively coupled plasma optical emission spectroscopy (ICP-OES) revealed that a > 40 % lithium leaching efficiency was achieved at an acid concentration of 8 M, a temperature of 100 °C, a residence time of 8 h, and a liquid to solid ratio of 10 mg/L. With further optimization, the leaching method could prove promising for lithium extraction from spodumene as well as other lithium-bearing silicates, such as lepidolite, zinnwaldite, and petalite.

Keywords: lithium extraction, spodumene, acid leaching, phosphoric acid, leaching mechanism

1. Introduction

In recent years, lithium has been labeled a critical element due to the prevalence of lithium-ion batteries in modern technology (European Commission, 2020; Greim et al., 2020; Natural Resources Canada, 2022). Increasing demand for lithium is expected to continue as the world transitions towards low-carbon technologies to maintain international agreements for sustainability (Tabelin et al., 2021). As such, devising sustainable methods to increase the availability of lithium from primary sources is of high priority.

Lithium is primarily sourced from brines, accounting for over 60 % of lithium production (Tadesse et al., 2019). The second largest source is from hard-rock deposits, with the main lithium-bearing minerals of interest being spodumene, petalite and lepidolite. Spodumene is the most widely processed in industry, as it has a comparatively high lithium grade and relative abundance (Tadesse et al., 2019). Despite its prominence, the current methods for lithium extraction from spodumene are complex and energy intensive (Karrech et al., 2020).

Spodumene exists naturally as α-spodumene, which has a monoclinic crystal structure. This structure is hard and dense, limiting the amenability to direct leaching. To improve the potential for lithium extraction, spodumene concentrates are subjected to a permanent phase transformation by calcination at temperatures in the range of 850 ºC to 1100 ºC (Pickles & Marzoughi, 2022; Salakjani et al., 2016). Calcination causes the crystal structure to expand by 30 % as it adopts the tetragonal structure of β-spodumene. The volumetric expansion decreases the bulk density, facilitating subsequent chemical attack.

Following calcination, β-spodumene is roasted in concentrated sulphuric acid at 250 ºC for 2 h. During roasting, there is ion exchange between the hydrogen atoms of sulphuric acid and the lithium ions of spodumene, leading to the formation of soluble lithium sulphate according to Equation 1 (Salakjani et al., 2021).

$$\mathrm{Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2(s) + H_2SO_4(l) \rightarrow Li_2SO_4(aq) + Al_2O_3{\cdot}4SiO_2{\cdot}H_2O(s)} \qquad (1)$$

In practice, sulphuric acid is added at a 30 % to 150 % stoichiometric excess to ensure complete conversion to lithium sulphate (Lajoie-Leroux et al., 2018; Salakjani et al., 2021). Metal ion impurities in the leach solution are removed by precipitation with calcium hydroxide, sodium hydroxide, calcium carbonate and sodium carbonate to arrive at a final lithium carbonate product (Tran & Luong, 2015).

The considerable amount of high-temperature concentrated sulphuric acid required for roasting presents significant health and safety risks for operation. Purification of the leach solution by precipitation with sodium hydroxide and sodium carbonate also leads to the formation of large amounts of sodium sulfate salt of little value (Alhadad et al., 2023). Many alternatives to the sulphuric acid roasting process have been proposed. These include alkaline roasting, chlorination roasting, carbonizing, and fluorination (Grasso et al., 2022; Kuang et al., 2018; Rosales et al., 2016). Alkaline roasting, chlorination processes, and fluorination methods have also been proposed for direct extraction of lithium from α-spodumene to omit the calcination step (Fosu et al., 2022; Guo et al., 2017; Han et al., 2022; Rosales et al., 2022; Song et al., 2019). Currently, the proposed processes suffer from intensive downstream purifications, high costs, or energy requirements that do not justify their adoption over the sulphuric acid process

(Alhadad et al., 2023; Grasso et al., 2022). For further details on extraction techniques, readers are referred to several recent reviews: (Choubey et al., 2016; Fosu et al., 2020; Karrech et al., 2020; Li et al., 2019; Salakjani et al., 2021; Yelatontsev & Mukhachev, 2021).

This study investigates the application of phosphoric acid as an alternative leaching method. Similar to sulphuric acid, phosphoric acid is a polyprotic mineral acid. It is produced as 85 wt % H_3PO_4, known as orthophosphoric acid, and is used as a source of phosphates for fertilizers, detergents, and food additives. If the H_3PO_4 content is increased past 85 wt % by the evaporation of water, the acid molecules can join by condensation to form polyphosphoric acids, also known as condensed phosphoric acids (Gilmour, 2014). Condensed phosphoric acids have been shown to form stable soluble silica compounds of SiP_2O_7, which has led to their use in the dissolution of silicate clays such as kaolinite, mica, and feldspar (Hannaker & Qing-Lie, 1984).

Phosphoric acid has not yet been applied as a leaching agent for lithium extraction from spodumene. It has been applied for the enrichment of rare earth elements from bauxite residues (Deng et al., 2017; Li, Ye, et al., 2018; Tsakanika et al., 2022), nickel and cobalt recovery from limonitic laterites (Li, Zhou, et al., 2018; Luo et al., 2021) as well as aluminum and iron impurity removal from graphite concentrates (Oh, 2022). It has also been applied to recover lithium and cobalt from waste cathode ($LiCoO_2$) of spent lithium-ion batteries (Chen et al., 2017; Pinna et al., 2017). In all studies, phosphoric acid was shown to be an effective leaching agent. With the exception of bauxite, all studies achieved extraction efficiencies in excess of 80 % for the metals of interest.

2. Materials and methods

2.1 Materials

Pure spodumene used for this work was purchased from Excalibur Mineral Corp (USA). The mineral specimens were crushed to ~25 mm using a hammer. The crushed sample was then stage pulverized to 100% passing 1.18 mm using a Labtechnics LM2 Laboratory Pulverizing Mill (Australia). The sample was wet screened using a 38 μm sieve. The -38 μm material was dried and homogenized to produce the feed for the leaching experiments.

The particle size distribution was determined to have a 50% passing size of 25.89 μm using a Microtrac Series 5000 Sync Particle Size & Shape Analysis system (Microtrac Inc, USA). Approximately 1 g of representative sample was prepared as a slurry with reverse osmosis water. For each test, approximately 2-3 drops of slurry were added into the machine. Sonication was done for 60 s to ensure complete dispersion before taking measurements.

ACS grade orthophosphoric acid containing 85 % w/w H_3PO_4 used in the leaching experiments was purchased from Fisher Scientific (USA). ACS grade nitric acid containing 70 % HNO_3 used for the digestion of solid samples for characterization was purchased from Sigma-Aldrich (USA). Sodium tetraborate flux and ammonium iodide tablets used for solid sample fusion was purchased from Malvern Panalytical (UK).

2.2 Calcination

The virgin sample was heated at 1100 °C for 4 h in a Thermolyne FB1415M Compact Benchtop Muffle Furnace (Thermo Fisher Scientific, USA) to convert α-spodumene to β-spodumene. The sample was placed in the furnace after the furnace was first preheated to 1100 °C. Heating was considered to be officially started once the furnace returned to 1100°C. After 4 h had elapsed, the furnace was turned off and the sample was left inside to cool to room temperature.

2.3 Leaching

Leaching experiments were conducted in triplicate on 1 g subsamples of calcined spodumene. The phosphoric acid solution for each experiment was adjusted to the desired volume and concentration with reverse osmosis water. Experiments were done in 15 mL digestion tubes heated continuously by a Touch Screen Dry Bath (ThermoFisher Scientific, USA). The tubes were mixed using a vortex mixer every 2 h of leach time up to 8 h. Once complete, the leach slurry was vacuum filtered in a filter flask with a ceramic Buchner funnel using Whatman Q8 filter paper. The leach filtrates and residues were kept for analysis.

2.4 Sample characterization

X-ray diffraction (XRD) was used to verify the phase transformation of spodumene following calcination, as well as the mineral phases present in the leach residues after leaching. XRD was carried out with a Bruker D8 Discover Diffractometer (USA) equipped with a Co Kα X-ray source (λ = 1.79 Å). Diffraction patterns were analyzed using DIFFRAC.EVA software (Bruker, USA). The measured XRD spectra for the virgin sample (Figure 1a) and leach feed (Figure 1b) indicated the complete conversion of α-spodumene to β-spodumene.

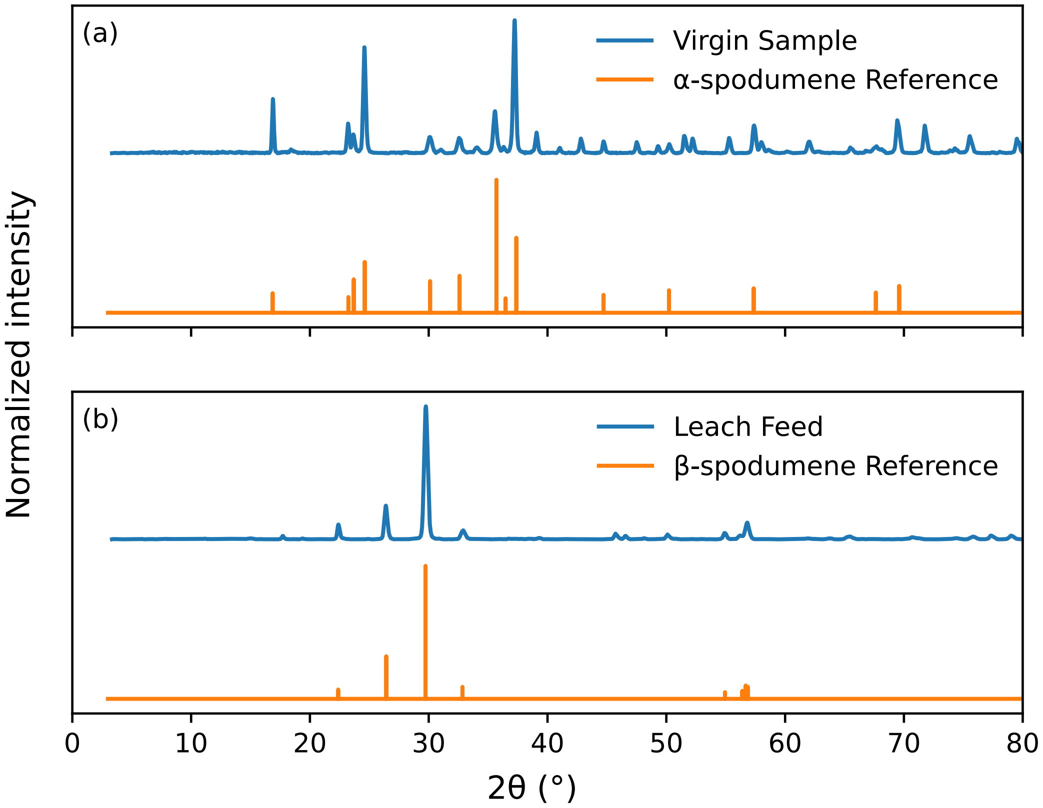

Figure 1. XRD patterns of virgin spodumene (a) and leach feed (b) compared to α- and β-spodumene references.

The lithium, aluminum, and silicon concentration in the leach feed, filtrates, and residues were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Thermo Scientific iCAP 6000 series ICP Spectrometer (USA).

To digest the solid samples, a homogenous melt was formed by heating 0.2 g of sample with 2 g of sodium tetraborate flux and a 0.03 g ammonium iodide tablet in a Pt-Au crucible. A programmed heating cycle was applied using a NIEKA E1 Electric Furnace. The amorphous melt was then digested in 15 % w/w nitric acid.

The composition of the leach feed determined by ICP is shown in Table 1.

Table 1. Chemical composition of the leach feed (error indicates 95 % confidence interval).

Element	Li	Al	Si
wt%	3.83 ± 0.12	13.13 ± 0.63	28.22 ± 0.82

3. Results and Discussion

3.1 Influence of leaching parameters on lithium extraction

The design of any commercial leaching process requires an evaluation of key leaching parameters which include temperature, leaching reagent type and concentration, residence time, particle grind size, stirring speed and liquid to solid ratio (Salakjani, 2021). For this preliminary study, the effects of phosphoric acid concentration, leaching temperature, leaching time, and liquid to solid ratio on the extraction of lithium, aluminum and silicon were investigated. These parameters were adjusted one-factor-at-a-time (OFAT) during the leaching experiments to assess (1) the feasibility of lithium extraction, and (2) the levels of the factors at which extraction was most pronounced. The particle size was kept fine so that the surface area to volume ratio of the spodumene particles was maximized. This was done to ensure that the leaching mechanism under investigation was not limited by insufficient acid-particle contact. Intermittent stirring was conducted for the same reason.

The extraction of each element was evaluated according to Equation (2)

$$Extraction\ (\%)\ =\frac{m_i^{filtrate}}{m_i^{leach\ feed}}\cdot 100\% \tag{2}$$

where $m_i^{filtrate}$ is the mass of element *i* that reported to the leach filtrate and $m_i^{leach\ feed}$ is the total mass of the element present in the leach feed.

3.1.1 Effect of phosphoric acid concentration

The effect of phosphoric acid concentration on leaching performance was investigated in a concentration range of 2 to 8 M at a temperature of 100 °C, a residence time of 4 h, and a liquid to solid ratio of 10 mL/g (Figure 2).

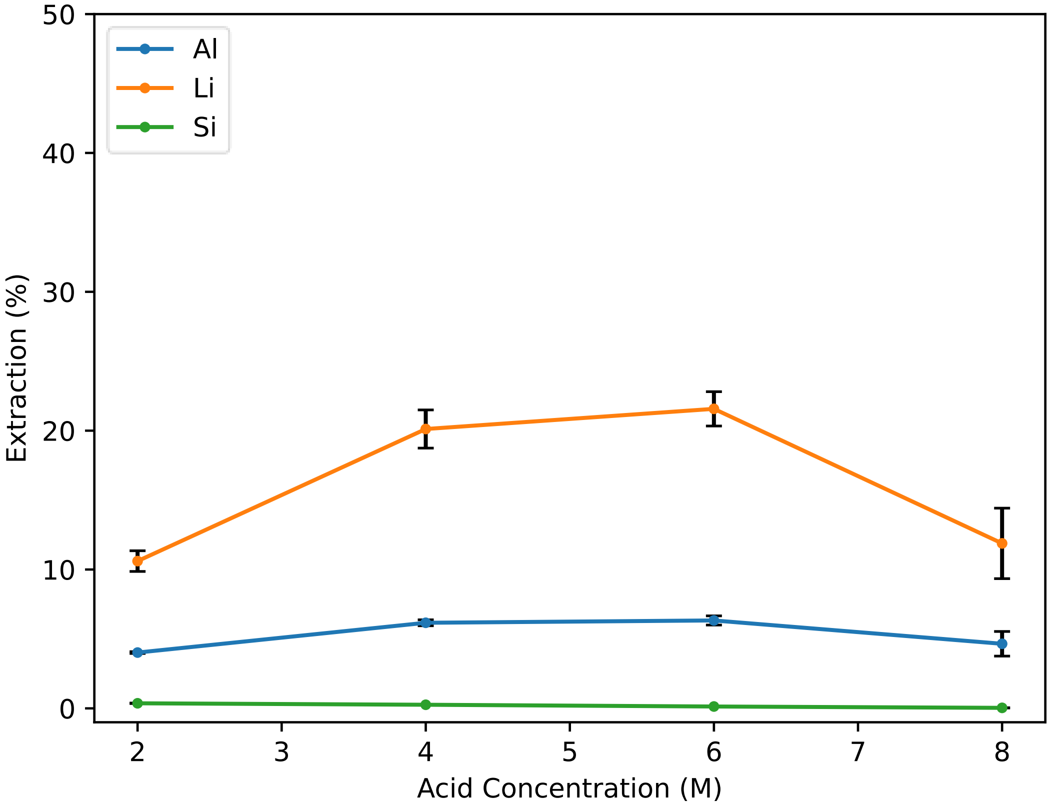

Figure 2. Effect of phosphoric acid concentration on extraction of Al, Li, and Si from spodumene (error bars indicate 95 % confidence intervals)

Li and Al extraction was highest between 4 and 6 M. At 8 M, extraction of Li and Al decreased to a similar level observed at 2 M. This decrease in leach performance could be a result of the increased viscosity of the concentrated acid limiting the mobility of ions in solution as observed by Tsakanika et al. (2022). At all phosphoric acid concentrations studied, Si extraction was negligible.

3.1.2 Effect of temperature

The effect of temperature on leaching performance was investigated from room temperature (21.3 °C) up to 100 °C at an acid concentration of 8 M, a residence time of 4 h, and a liquid to solid ratio of 10 mL/g (Figure 3). The boiling point of orthophosphoric acid is 158 °C; therefore, the upper limit was chosen to be 100 °C to avoid boiling of the diluted acid during leaching.

The extraction of all elements was negligible below 50 °C. At 75 °C, extraction of Li and Al started to increase, and continued to increase at 100 °C. This trend indicates that higher extraction could be achieved at higher temperatures. At all temperatures studied, Si extraction was negligible.

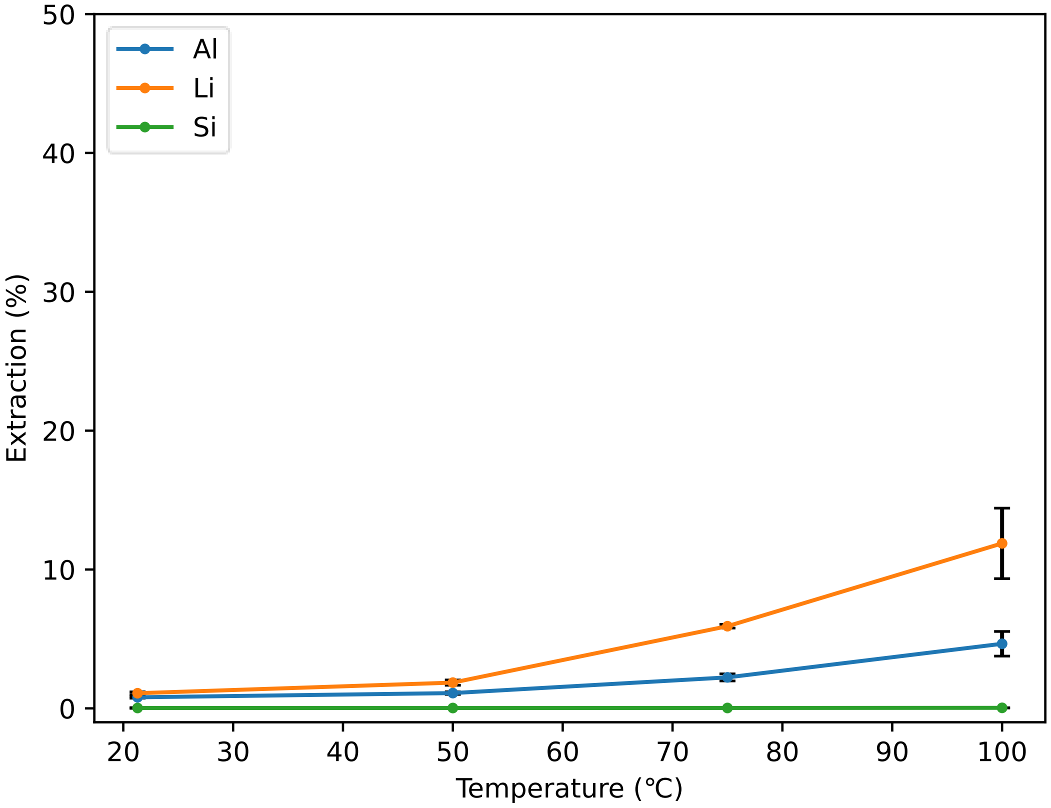

Figure 3. Effect of temperature on extraction of Al, Li, and Si from spodumene (error bars indicate 95 % confidence intervals)

3.1.3 Effect of residence time

The effect of residence time on leaching performance was investigated in a range of 2 to 8 h at an acid concentration of 8 M, a temperature of 100 °C, and a liquid to solid ratio of 10 mL/g (Figure 4).

Increasing residence time had the most noticeable impact on Li extraction. Li extraction of 42 %, the highest lithium extraction achieved out of all the leaching conditions investigated, was reached after a leach time of 8 h. The corresponding aluminum and silicon extractions were 9.1 % and 0.1 %, respectively.

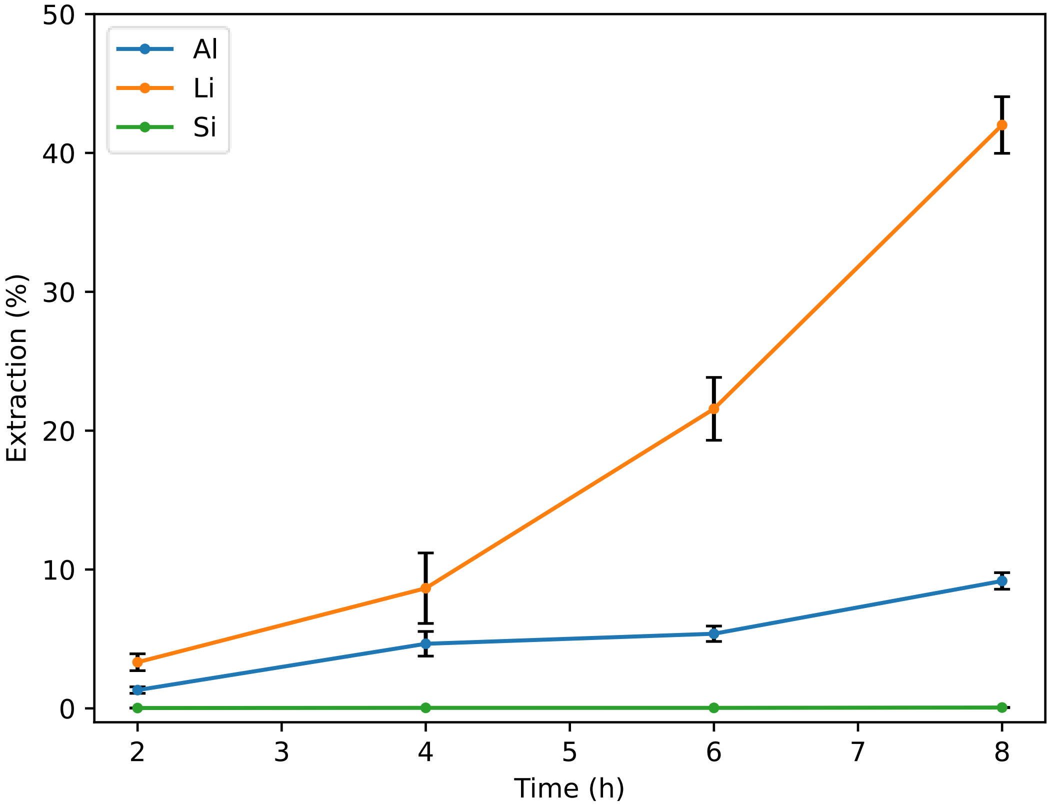

Figure 4. Effect of residence time on extraction of Al, Li, and Si from spodumene (error bars indicate 95 % confidence intervals)

The trends for Li and Al extraction increased continuously for the residence times investigated, with no discernible plateau. Additional experiments with residence times of 16 h and 24 h were conducted to verify if Li extraction could be increased further. ICP results for these experiments have not been obtained at the time of draft submission but are planned to be included once available.

3.1.4 Effect of liquid to solid ratio

The effect of liquid to solid ratio on leaching performance was investigated in a range of 4 to 10 mL/g at an acid concentration of 8 M, a temperature of 100 °C, and a residence time of 4 h (Figure 5).

Al extraction decreased to what appeared to be a lower plateau of approximately 4 % past 6 mL/g. Li extraction decreased continuously for the residence times investigated. However, there was no discernible plateau below 4 mL/g, and there appeared to be the beginning of a plateau at high values. Additional experiments with liquid to solid ratios of 1 mL/g and 15 mL/g were conducted to verify the extraction at extreme limits. ICP results for these experiments have not been obtained at the time of draft submission but are planned to be included once available.

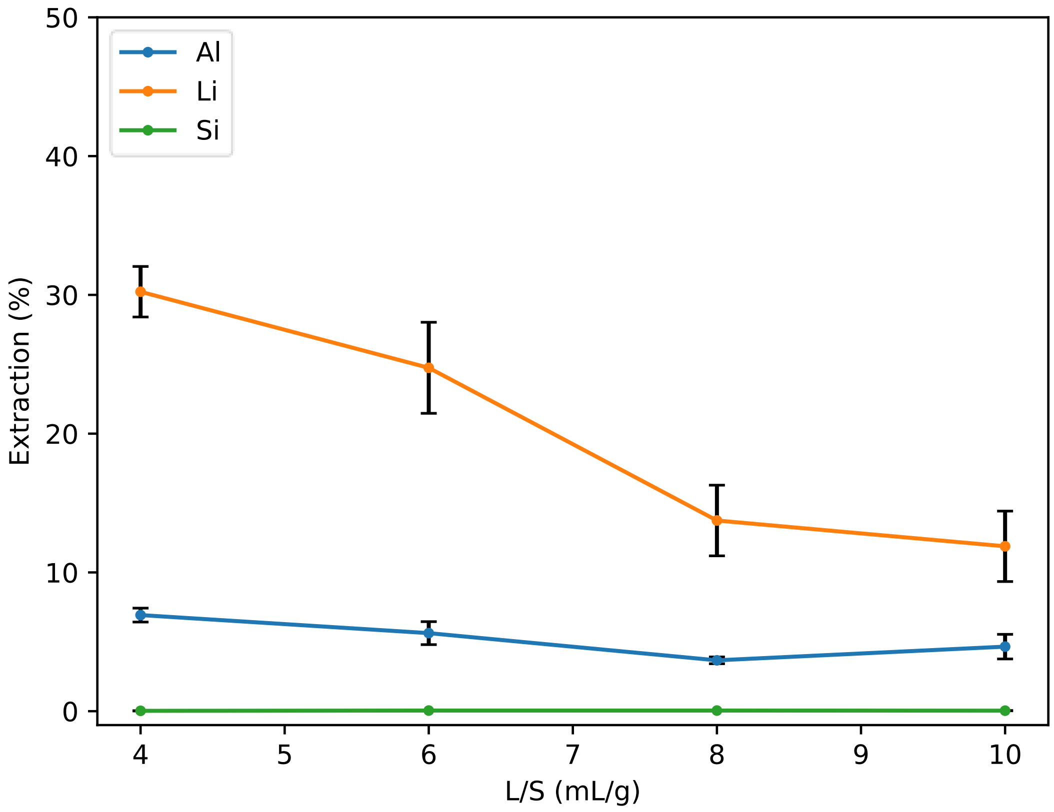

Figure 5. Effect of liquid to solid ratio on extraction of Al, Li, and Si from spodumene (error bars indicate 95 % confidence intervals)

Moreover, a liquid to solid ratio of 1 mL/g was found to be too low for practical leaching as it did not fully wet the particle surface. The final leach sample was ten times diluted in order to have enough filtrate for ICP analysis. A liquid to solid ratio of 15 mL/g would also be considered impractical from an industrial point of view due to the significant amount of acid volume and leach tank size required to process low amounts of spodumene concentrate.

3.2 Proposed reaction mechanisms

The polyprotic nature of phosphoric acid leads to stepwise ionization (Equation (3) to Equation (5)) with the following acid ionization constants (K_a):

$$\mathrm{H_3PO_4} = H^+ + H_2PO_4^- \tag{3}$$

$$K_{a1} = 7.5 \cdot 10^{-3}$$

$$H_2PO_4^- = H^+ + HPO_4^{2-} \tag{4}$$

$$K_{a2} = 6.2 \cdot 10^{-8}$$

$$HPO_4^{2-} = H^+ + PO_4^{3-} \tag{5}$$
$$K_{a3} = 4.8 \cdot 10^{-13}$$

The species distribution is dependent on the solution pH, where pH is related to K_a by Equation (7):

$$pH = -log(K_a) \tag{6}$$

The leaching experiments were conducted in very acidic conditions (pH < 2), indicating that the predominant species present in the reaction is the single protonated species ($H_2PO_4^-$). This suggests that the chemical reaction for leaching with phosphoric acid could be driven by ion-exchange between H and Li by Equation (7), similar to the reaction with H_2SO_4 (Equation (1)).

$$Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2(s) + 2\ H_3PO_4(l) \rightarrow 2\ LiH_2PO_4(aq) + Al_2O_3{\cdot}4SiO_2{\cdot}H_2O(s) \tag{7}$$

This theory is supported by the observation of the same delithiated aluminum silicate corresponding to leached spodumene (Botto, 1985; Salakjani et al., 2019) in the XRD spectra of the residues from experiments with high extraction (Figure 6). Figure 7 shows the gradual formation of this delithiated aluminum silicate with increasing residence time.

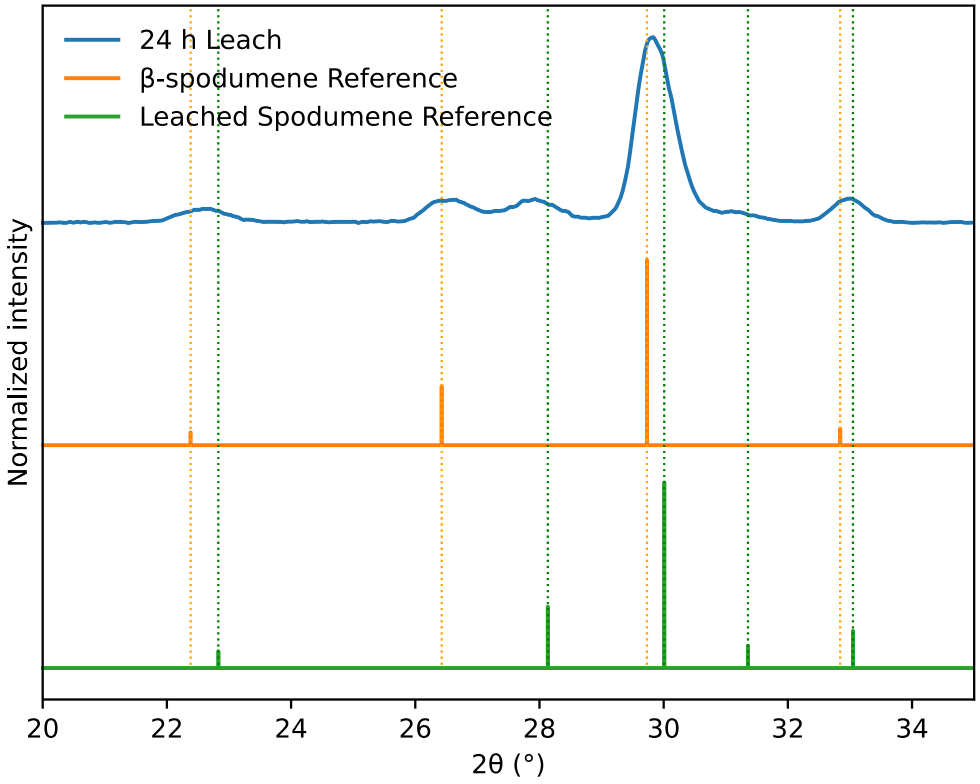

Figure 6. Magnified XRD spectrum of leach residue after leaching for 24 h at 8 M, 100 °C and 10 mL/g compared to β-spodumene and leached spodumene references.

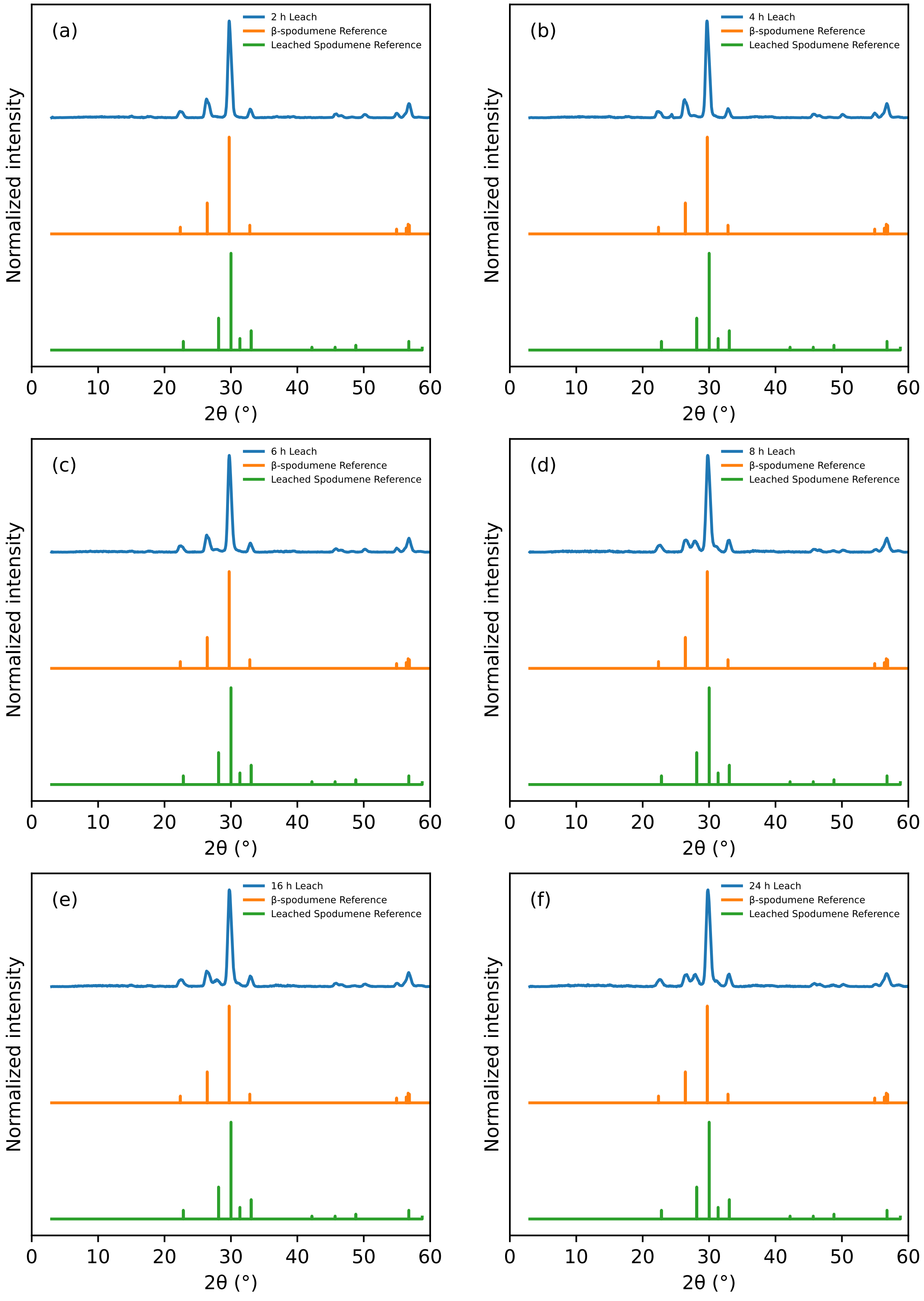

Figure 7. XRD spectra of leach residues from experiments conducted at 8 M H_3PO_4, 100 °C, and 10 mL/g with residence times of (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, (e) 16 h, and (f) 24 h.

4. Conclusions

In this study, the application of phosphoric acid under mild conditions was considered as an alternative leaching agent for lithium extraction from β-spodumene. Phosphoric acid was found to selectively leach lithium from aluminum and silicon.

Lithium extraction increased with increasing temperature, increasing residence time, and decreasing liquid to solid ratio. Phosphoric acid concentration had a negative quadratic effect, with optimal extraction occurring between 4 to 6 M. A maximum lithium extraction of 42 % was achieved at an acid concentration of 8 M, a temperature of 100 °C, a residence time of 8 h and a liquid to solid ratio of 10 mL/g. The corresponding aluminum and silicon extraction were 9.1 % and 0.1 %, respectively.

The lithium extraction achieved in this study was low compared to other methods that have been reported. However, the relatively mild operating conditions and absence of sulphate ions in the process offer a sustainable alternative to the conventional sulphuric acid roasting process. Additionally, the independent trends of the parameters studied indicated that optimization of the system could result in significantly higher extraction.

It is generally understood that the results from OFAT experiments are limited, as they do not consider the interactions between factors (Czitrom, 1999). Using the effective parameter ranges that have been defined in this study, future work will aim to optimize the leaching conditions by response surface methodology, which is expected to account for these limitations.

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